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SYNTHESIS OF ENERGETIC POLYMERS

Summary Report
15 July 1980 to 14 July 1981

October 15, 1981

By: G. E. Manser and D. L. Ross

Prepared for:

OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, Virginia 22217

Attention: Dr. Richard S. Miller
Code 473

Contract No. N00014-79-C-0525; NR093-063

SRI Project PYU 8627

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Three general synthetic routes to the preparation of energetic oxetanes and tetrahydrofurans were investigated during the first year of the program. Subsequently, 3-(2-fluoro-2,2-dinitroethyl-3-methyloxetane (FOE) was prepared and polymerized to give oligomers with molecular weights ranging from 6,000 to 15,000. Efforts to develop a general synthetic route to 3-nitroalkyl substituted oxetanes starting with methylene malonate were not successful. However, work		

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Work on a general route to nitroalkyl-substituted tetrahydrofurans resulted in 3-(2,2-dinitropropyl)tetrahydrofuran (3-DNP THF), which was prepared using a synthetic route of general applicability to other 3-substituted tetrahydrofurans. A preliminary polymerization study yielded dimer and trimer, suggesting that polymerization was possible.

At this point of the program it was evident that even if a series of cyclic ether monomers were available, the state-of-the-art of cationic polymerization techniques was inadequate to permit us to obtain polyols with the requisite properties without additional research. Consequently, further research resulted in a significant breakthrough in polymerization techniques as they apply to the preparation of polymers for propellant and explosives applications. By use of a 2/1 borontrifluoride/alkanediol complex we were able to control the initiator/monomer ratio to obtain a polyol of predetermined molecular weight and narrow polydispersity. The resulting polymer molecular weight was equal to the stoichiometric addition of the molecular weights of the diol and monomer. Functionality of the polymer was the theoretical value (2) with minimal cyclic oligomer contamination.

3,3-Bis(azidomethyl)oxetane (BAMO) was used to investigate the effect of polymer molecular weight on melting point of resultant polymers as this property is important with respect to formulation. However, it became evident that the melting point of BAMO homopolymer (76° to 78°C) was not influenced by varying the molecular weight. Thus, to lower the melting point (crystallinity) of the BAMO polyols, we investigated the copolymerization of BAMO with tetrahydrofuran (THF). We found that a melting point as low as -5°C could be achieved in a 50/50 mol% BAMO/THF copolymer. The physical and elastomeric properties of the copolymer were examined both in the cured and uncured state. The test results indicate that the copolymer is a viable candidate energetic prepolymer with excellent physical properties that meet the following criteria:

- Moderate energy
- Reproducible molecular weight (2,000 to 4,000)
- Low polydispersity (1.1 to 1.2)
- Functionality of 2
- Liquid at room Temperature
- Glass transition temperature -54°C.

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The syntheses of 3-azidomethyltetrahydrofuran, 3,4-bis(azidomethyl) tetrahydrofuran, and 2-azidomethyltetrahydrofuran were completed for use as replacements for tetrahydrofuran to increase the energy of BAMO copolymers relative to the BAMO/THF copolymer.

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PUBLICATIONS, PATENTS AND PRESENTATIONS

May 12, 1981, Patent Application No. 262935 filed

"Cationic Polymerization"

May 26, 1981

Paper presented at the 1981 JANNAF Propulsion meeting, New Orleans, Louisiana:

"A Technique for Preparing Low Molecular Weight Polyether Glycols"

July 21, 1981

Paper presented at 1981 Symposium on the Chemistry of Synthesis and Characterization of Energetic Monomers and Polymers, The Johns Hopkins University, Laurel, Maryland:

"BAMO/THF Copolymer: A Candidate Energetic Polyether Glycol"

September 1981

Submitted to the Journal of Polymer Sciences for publication:

- The Controlled Cationic Polymerization of Cyclic Ethers
- Copolymerization of 3,3-Bis(azidomethyl)oxetane and Tetrahydrofuran

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We also wish to acknowledge the valuable suggestions and encouragement of Dr. P. A. Miller, Project Consultant and Dr. R. S. Miller, ONR Project Monitor.

SUMMARY

Three general synthetic routes to the preparation of energetic oxetanes and tetrahydrofurans were investigated during the first year of the program. Subsequently, 3-(2-fluoro-2,2-dinitroethyl-3-methyloxetane (FOE) was prepared and polymerized to give oligomers with molecular weights ranging from 6,000 to 15,000.

Efforts to develop a general synthetic route to 3-nitroalkyl substituted oxetanes starting with methylene malonate were not successful. However, work on an alternative general route to oxetanes afforded oxetane 3,3-diacetic acid in low yield. This material could be used to prepare a series of nitro esters of oxetane, but this work was terminated as our experience has shown that cationic polymerization of esters does not produce significant conversion of the monomer.

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At this point of the program it was evident that even if a series of cyclic ether monomers were available, the state-of-the-art of cationic polymerization techniques was inadequate to permit us to obtain polyols with the requisite properties without additional research.

Consequently, further research resulted in a significant breakthrough in polymerization techniques as they apply to the preparation of polymers for propellant and explosives applications. By use of a 2/1 borontrifluoride/alkanediol complex we were able to control the initiator/monomer ratio to obtain a polyol of predetermined molecular weight and narrow polydispersity. The resulting polymer molecular weight was equal to the stoichiometric addition of the molecular weights of the diol and monomer. Functionality of the polymer was the theoretical value (2) with minimal cyclic oligomer contamination.

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- Moderate energy
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- Low polydispersity (1.1 to 1.2)
- Functionality of 2
- Liquid at room temperature
- Glass transition temperature, -54°C.

Four methods of preparing the copolymer were examined in an effort to optimize the polymerization reaction and final physical properties. Extensive kinetic data have been obtained for both the homopolymerization of BAMO and the copolymerization of BAMO with THF.

The syntheses of 3-azidomethyltetrahydrofuran, 3,4-bis(azidomethyl)tetrahydrofuran, and 2-azidomethyltetrahydrofuran were completed for use as replacements for tetrahydrofuran to increase the energy of BAMO copolymers relative to the BAMO/THF copolymer.

DISCUSSION

A. Introduction

The major effort during the second year was concerned with developing new polymerization techniques that can be used to control the physical properties and molecular weights of polymers derived from the cationic polymerization of oxetanes and tetrahydrofurans.

Our experience as well as published data show that the cationic polymerization of oxetanes is difficult to control because of high monomer reactivity. We found that the published⁽¹⁻⁴⁾ techniques used to lower molecular weights have little effect in the system that we investigated. In fact, the techniques are not sufficient to obtain reproducible molecular weights from batch-to-batch. Previous techniques have included use of dilute solutions, high catalyst loading, water as a cocatalyst, high temperatures, and quenching at low polymer yields. However, we concluded that even if a large number of candidate energetic oxetanes and tetrahydrofurans become available, the state-of-the-art of cationic polymerizations is inadequate to permit us to obtain polymers with the requisite properties without additional research.

High molecular weights are obtained if a small number of initiating species is formed during polymerization. However, since our objective is to achieve relative low molecular weights (2000 to 4000), our research has been concerned with increasing the number of initiating species. We have found that the molecular weight is limited by the ratio of monomer units to initiating species. That is, when the catalyst (boron trifluoride in most cases) is added to an oxetane and alkanediol mixture, the catalyst preferentially reacts with the diol to form an "adduct" that initiates polymerization. Because the resultant molecular weight is inversely proportional to the adduct concentration, we have therefore demonstrated an accurate technique to vary and predict molecular weight by varying the number of initiating species.

B. Homopolymerization

A series of polymerizations was completed using various ratios of oxetane to diol. Initially we used 3-methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE) as the oxetane monomer and 2-(2,2-dinitropropyl) butane-1,4-diol as the diol. In a series of three polymerizations the molecular weights of the resultant polymers were the same as the sum of the molecular weights of the ratio of oxetane and diol initially present. The polymers were obtained in >90 wt% conversion, based on monomer, and had very narrow molecular weight distributions (low polydispersity).

To rapidly explore a system that could possibly meet the Navy's short term goals, we concentrated on developing a polyol based on 3,3-bis(azidomethyl) oxetane (BAMO). This monomer was selected as it is readily prepared in large quantities at relatively low cost compared to other known energetic monomers. By increasing the polymerization scale from 0.4 g to 10 g and using 1,4-butanediol/BF₃.Et₂O in a 1/2 mole ratio as the initiating species, we achieved the molecular weight control previously observed with FOE. Furthermore, on purification, the polydispersity, as determined by gel permeation chromatography, was 1.1-1.3.

A series of BAMO polymerizations was conducted to produce a range of molecular weights for determination of the relationship of melting point to molecular weight. We found that a polyol derived from BAMO of molecular weight 3000 melts at 78°C. In varying the molecular weight from 1500 to 6500 little change in melting point was observed (76° to 80°C). Considering the technique now used for cast-cured systems, the melting points of these polyols are at the upper limit of that considered practical.

C. Copolymerization

Because the melting point of poly-BAMO could not be lowered by lowering the molecular weight, we shifted our research to the copolymerization of BAMO. The physical properties of macromolecules are dependent on the crystallinity of the system, which in turn is directly proportional to the symmetry of the repeating unit. Therefore, it is reasonable to expect that

a homopolymer will tend to be more crystalline than a copolymer containing a dissimilar monomer. Also, the more random the repeating unit placement is in the copolymer, the less crystalline the copolymer. This lower crystallinity will lower the melting point and glass transition temperature and increase the overall flexibility of the final polyol.

With the above reasoning in mind, we conducted a series of copolymerizations of BAMO with THF. Our investigation of two systems, namely 75/25 and 50/50 mole % BAMO/THF, show a dramatic lowering of melting point:

Polyol, BAMO/THF, mole %	Molecular Weight, \bar{M}_w	Melting Point, °C	Density, g/cc	ΔH_f , kcal/100 g est.	f
100/0	6500	78	1.3	+60	1.92
75/25	6900	50	1.245	+42	1.96
50/50	7300	<0	1.180	+17	1.99

At a molecular weight of 6900 a melting point of 50°C was observed for the 75/25 system whereas the 50/50 system is a flowable oil at room temperature. The 75/25 mol% BAMO/THF is comparable in melting point to PEG 4000 (mp 55°C). Although THF is a nonenergetic monomer, the calculated heats of formation of the copolymers are still favorable. The functionalities of the copolymers were almost the theoretical value of 2.0.

C. Scale up of BAMO/THF Copolymer

The 50/50 mol% BAMO/THF polymer was selected for scale up and subsequent formulation to a cured gumstock. As stated previously, the 50/50 mol% BAMO/THF copolymer is a mobile oil at ambient temperature and its viscosity is relatively low compared to polymers with higher BAMO content. We found that stirring became easier as the batch size increased, whereas viscosity was more troublesome on a small scale. Polymerization temperature is considered the most important parameter for high monomer conversion. It is known⁽⁵⁾ that the conversion of THF to polymer is 89% at 0°C, 72% at 30°C

and 0% at the ceiling temperature of 85°C. Although our initial work was conducted at -20°C, we found that -5°C produces identical material. As a bonus, the polymerization viscosity is lowered somewhat at the higher temperature. While maintaining the polymerization temperature at -5°C we examined four methods of polymer preparation.

First we prepared the initiator by reaction of butanediol with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in THF and then added BAMO to the THF solution over a 15-minute period. A rapid uptake of BAMO and THF was observed over the first hour at which point the rate of THF uptake decreased. After 5 hours 75% BAMO and 55% THF had been converted. After 20 hours BAMO had reached a steady state of 98% conversion whereas THF reached a steady state of 85% after 38 hours. Based on the amount of monomers remaining, the final polymer composition was calculated to be 56% BAMO/44% THF.

Due to the difference in reactivity of THF and BAMO one could expect that the head of the polymer chain would rich in BAMO and the tail rich in THF, however, during the middle 60% of the polymerization time a 1:1 monomer uptake was observed.

A second method of preparation was examined in order to achieve a more random copolymer: BAMO was added dropwise to the THF initiator solution over the entire run of 42 hours. In this case nearly 3 hours passed before BAMO was in high enough concentration to take part in the polymerization, whereas 30% of the THF had polymerized. However, once BAMO began to polymerize the ratio of monomer uptake was 1:1. This rate of uptake continued for 23 hours at which time the THF level decreased to a point where BAMO homopolymerization predominated. After 45 hours, a steady state was achieved, indicating a final 87% THF and 96% BAMO uptake. The resultant polymer was similar to that obtained when BAMO and THF were added simultaneously, that is, a head rich in BAMO and a tail rich in THF. It should be noted that because THF was in excess during most of the run, the polymerization viscosity was relatively low until the final 2 hours when the viscosity approached that observed in the previous run.

A third method, namely solution polymerization, was examined in an attempt to reduce the polymerization viscosity. It is well known⁹ that oxetanes readily polymerize in solution whereas tetrahydrofuran polymerization is hindered. THF homopolymerization to 90% conversion is attained in bulk, but only a 27% conversion is achieved at room temperature in a 60% dichloromethane solution. However, the use of nitromethane is reported⁽⁵⁾ to effect higher conversions. Consequently a BAMO/THF copolymerization was run in nitromethane. After 24 hours, analysis showed that the polymerization had achieved a steady state of 98% conversion of BAMO and 52% of THF. We conclude that solution copolymerization of BAMO/THF will require further investigation if the need arises.

A fourth method of polymerization was examined in which all monomers and catalyst were stirred at -5°C for 30 minutes and then allowed to polymerize for 40 hours without further stirring. After quenching, the resulting polymer was found to be identical in all respects to those obtained previously. As this method of polymerization alleviates the problems associated with stirring increasingly viscous material it is considered the method of choice for scale-up.

D. Gumstock Preparation and Testing of 50/50 mol % BAMO/THF Polymer

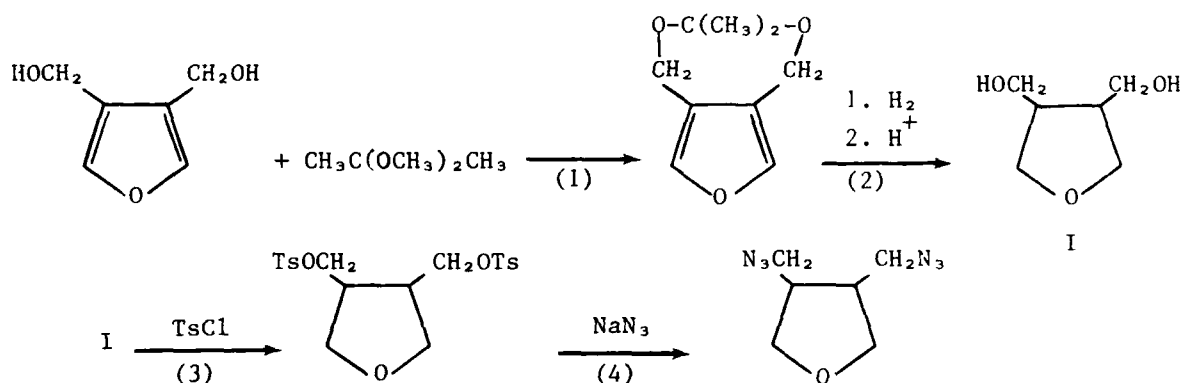
Gumstocks were prepared from bulk-polymerized 50/50 BAMO/THF polymers. The polymer was mixed with trimethylolethane to achieve the required crosslink density and then with one equivalent of tolylene diisocyanate, which is the amount required to give an infinite network. After curing 24 hours at 65°C the samples were subjected to various tests.

The stress/strain curve, obtained by Instron measurement, gave a value of 115 psi at 425% elongation at a crosslink density of 10%. An average of 89,000 molecular weight between crosslinks was determined by swelling experiments. A Rheovibron study showed a classical E' curve for an elastomer from -80°C to room temperature and the E'' curve showed a single deflection at -54°C corresponding to the glass transition temperature. Differential scanning calorimetry showed a flat trace until the onset of an exotherm starting at 210°C and maximizing at 254°C. Samples of polymer and gumstocks have been distributed to other investigators for further studies.

E. Alternative Monomers

To provide energetic replacements for THF, the synthesis of three substituted tetrahydrofurans was investigated: 3,4-bis(azidomethyl) tetrahydrofuran, 3-azidomethyl tetrahydrofuran, and 2-azidomethyl tetrahydrofuran.

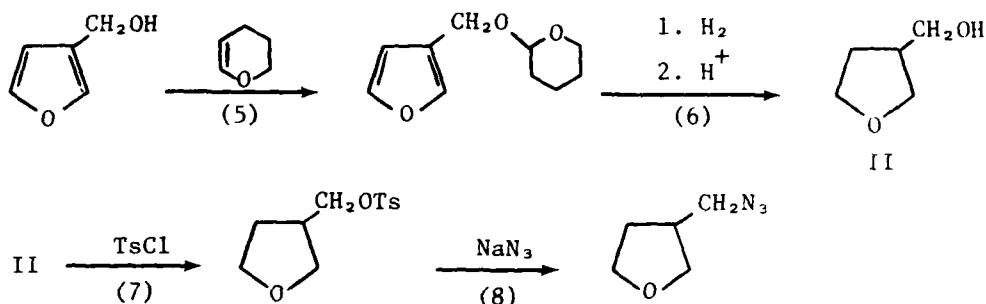
3,4-Bis(azidomethyl) THF is prepared by the following sequence of reactions, equations (1) through (4).



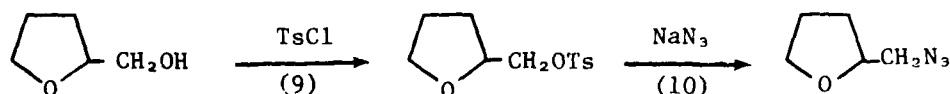
Equations (1) through (3) are described by Gatos⁽⁶⁾. The replacement of the tosyl groups with azido groups, equation (4), was accomplished in dimethyl sulfoxide (DMSO). The desired product distilled at 81°C (0.01 Torr) to give a clear colorless liquid in 80% yield (based on the tosylate).

Attempts to prepare 3,4-bis(azidomethyl) tetrahydrofuran via reaction of sodium azide with bis(chloromethyl) tetrahydrofuran were not successful.

The preparation of 3-azidomethyl tetrahydrofuran follows that of the bis(azidomethyl) tetrahydrofuran, equations (5) through (8):



Equations (5) through (7) have been successfully completed and the products have been characterized. Reaction (8) was attempted using DMSO as the solvent; a clear, colorless liquid was isolated, b.p. 72°C/15 torr. Analysis of the product indicates a stable complex composed of 2 parts 3-azidomethyl tetrahydrofuran and 1 part DMSO. The complex appears to be thermally stable as demonstrated by a single peak in the gc analysis (injector temperature 250°C). The reaction will be repeated in a different solvent to avoid the formation of a complex. However, rather than experiment with 3-azidomethyl THF in searching for an appropriate solvent we chose to examine 2-azidomethyl tetrahydrofuran. Our reasons for using the 2-azidomethyl tetrahydrofuran are: (a) 2-azidomethyl tetrahydrofuran is easily prepared from the inexpensive tetrahydrofurfural alcohol, equations (9) and (10); (b) we are interested in determining if 2-substituted-THF's can be copolymerized; and (c) DMSO may not form a complex with the 2-azidomethyl-THF.



2-Azidomethyl-THF was prepared from the tosylate in DMSO, as shown in equations (9) and (10). Unfortunately, a stable, distillable 1:1 complex of

2-azidomethyl-THF and DMSO was obtained. It is interesting to note that 3,4-bis(azidomethyl)-THF does not form a DMSO complex, and 3-Azidomethyl-THF forms a 2:1 DMSO complex. Because the scope of the research did not permit detailed examination of this observation at the time we propose a more in-depth study later. A second attempt to prepare the 2-azidomethyl-THF using ethylene glycol as solvent gave the desired product in 67% yield based on the tosylate.

EXPERIMENTAL

A. 3,4-Bis(hydroxymethyl)tetrahydrofuran Bis(p-toluenesulfonate)

A solution of 38 g (0.02 mol) of p-toluenesulfonyl chloride in 50 mL of pyridine was added to a solution of 7.8 g (0.06 mol) 3,4-bis(hydroxymethyl) tetrahydrofuran in 100 ml of pyridine over a period of 15 min at 10°-20°C. The reaction mixture was stirred at ambient temperature for 18 hr and then poured into 500 ml of ice water. The aqueous solution was decanted from the gummy residue, which was then dissolved in methylene chloride. The methylene chloride solution was dried with magnesium sulfate and evaporated, leaving 8.5 g (32% yield) of product which was used without further purification.

B. 3,4-Bis(azidomethyl)tetrahydrofuran

A mixture of 8.5 g (19.3 mmol) of 3,4-bis(hydroxymethyl)tetrahydrofuran bis(p-toluenesulfonate), 7 g (107 mmol) of sodium azide, and 50 mL of DMSO was stirred at 65°C for 18 hr. The reaction mixture was cooled and poured into 200 ml of water, which was then extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated. The product was distilled at 81°C/0.01 Torr to yield 2.9 g product (82% yield). ir: 2060 cm^{-1} (s, N_3), 1260 (m, COC). nmr (CDCl_3): 2.5 (m, CHCH), 3.4 (d, CH_2OCH_2 , $J_{\text{Hz}} = 7$), 3.8 (m, CH_2N_3). Elemental analysis calculated for $\text{C}_6\text{H}_{10}\text{N}_6\text{O}$: C, 39.56; H, 5.53; N, 46.13. Found: C, 39.54; H, 5.47; N, 44.80.

C. Tetrahydrofuran p-Toluenesulfonate

A solution of 304 g (1.6 mol) of p-toluenesulfonyl chloride in 400 mL of pyridine was added to a solution of 96 g (0.94 mol) of tetrahydrofurfuryl alcohol in 400 ml of pyridine over a period of 1 hr at 10°-20°C. The reaction was stirred at ambient temperature for 4 hr and then poured into 3 L of water. The oil which separated was washed repeatedly with water until it

crystallized to a fine powder, which was filtered and dried in vacuum to yield 214 g of product (89% yield).

D. 2-Azidomethyl Tetrahydrofuran

A mixture of 102 g (0.4 mol) of tetrahydrofurfuryl p-toluenesulfonate (0.8 mol), sodium azide, and 300 ml of ethylene glycol was stirred at 80°C for 18 hours. The reaction mixture was cooled and poured into 2 L of water, and the product was extracted with three 300-mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated leaving 47 g of crude product, which was distilled at 54°/4 Torr to yield 35.6 g (70%) pure product. ir: 2110 (s, N₃), 1090 cm⁻¹ (m, COC). nmr (CDCl₃): 1.9 (m, CH₂CH₂), 3.3 (m, CH₂N₃), 3.9 (m, CH₂OCH) Elemental analysis calculated for C₅H₉N₂O: C, 47.23; H, 7.13; N, 33.06. Found: C, 47.12; H, 7.13; N, 31.24.

E. 3-Hydroxymethyl Tetrahydrofuran p-Toluenesulfonate

A solution of 15.25 g (0.08 mol) p-toluenesulfonyl chloride in 13 mL pyridine was added to a solution of 8.0 g (0.08 mol) 3-hydroxymethyl tetrahydrofuran in 10 ml pyridine dropwise at <10°C. The reaction mixture was stirred at 0°-5°C for 18 hrs and then at ambient temperature for 24 hr. It was then poured into ice water and stirred 30 min. The water was decanted from the organic phase which was dissolved in ether, washed with water, and dried over magnesium sulfate. The ether was evaporated leaving 10.6 g (52% yield) of product which was used without further purification.

F. 3-Azidomethyl Tetrahydrofuran

A mixture of 10.6 g (0.041 mol) of 3-hydroxymethyltetrahydrofuran p-toluenesulfonate, 2.7 g (0.04 mol) sodium azide and 50 mL DMSO was stirred at 65°C for 18 hr. The reaction mixture was cooled to ambient temperature and poured into 200 ml water. The aqueous solution was extracted with three 50-mL portions of methylene chloride, and the methylene chloride solution was dried over magnesium sulfate and evaporated leaving 4.1 g of crude product. The product was distilled at 69°/15 Torr to yield 3.1 g pure product (99.9% based

on GC analysis). The product appears to be a 2:1 complex of 3-azidomethyl THF and DMSO. Both the nmr and elemental analysis support this conclusion. ir: 2070 cm^{-1} (s, N_3), 1275 (m, S=O), 1055 (s, COC). nmr (CDCl_3) $1.9\ \delta$ (m, CH_2CH), 2.6 (s, CH_3), 3.3 (d, CH_2N_3 , $J_{\text{H}} = 8$), 3.8 (m, CH_2OCH_2). Elemental analysis calculated for $\text{C}_{12}\text{H}_{24}\text{N}_6\text{OS}$: C, 43.36; H, 7.28; N, 25.28. Found: C, 43.78, H, 7.15; N, 24.46.

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Appendix A

THE CONTROLLED CATIONIC POLYMERIZATION OF CYCLIC ETHERS

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SYNOPSIS

We have demonstrated that cationic polymerization of cyclic ethers can be controlled to give polyethers of predetermined molecular weight by adjusting the stoichiometry of initiator and monomer. The initiator is a complex of an alkanediol and a Lewis acid. The polymer molecular weights achieved are proportional to the sum of the molecular weights of the initiator diol and the monomer. The resulting polymers have a narrow polydispersity and a functionality of 2.

INTRODUCTION

The cationic polymerization of cyclic ethers to produce polyether glycols has been extensively investigated during the past fifteen years. Aside from the polymers derived from epoxides, poly(tetrahydrofuran) is the most widely produced polyether glycol of commercial interest. These polyethers are used as prepolymers in the preparation of polyurethanes. This application requires low molecular weights (2000 to 4000) and a hydroxy functionality of 2.

The objective of our research is to prepare energetic polyether glycols for formulation into energetic polyurethane binders for propellants and explosives. We have focused our research on the cationic polymerization of substituted oxetanes, and tetrahydrofuran, with the aim of preparing polyether glycols with molecular weights between 2000 and 4000, narrow polydispersities, and functionalities of 2.

The methods reported in the literature¹⁻³ for producing low molecular weight oligomers from cyclic ethers include using high catalyst loadings, high polymerization temperature, and cocatalysts. These techniques produce lower molecular weights by increasing the frequency of termination steps. In our hands these techniques produced a lower molecular weight, but also gave decreased monomer conversion, a decrease in functionality, and a marked increase in the formation of cyclic oligomers. The decreased monomer conversion required the separation of monomer from polymer, preventing practical scale-up, and polydispersities of greater than two were commonly observed in products produced by these methods.

We felt that a more satisfactory approach would be to choose an initiator that would produce a reaction mixture that was reasonably free of transfer and termination reactions. This would permit an increase in the initiator concentration and allow the molecular weight of the product to be controlled only by the amount of monomer available.

A review of the literature on stable BF_3 -initiator complexes⁴⁻⁸ indicated that the use of 1,4-butanediol did decrease the cyclic oligomer content of the product mixture. Cyclic oligomer formation is the most obvious termination reaction competing with the desired polymerization. Hammond's work¹⁰ suggested that the molecular weight was affected by the quantity of diol used, but his work did not address the distinction between conversion and diol content. In Hammond's work the catalyst and diol were only used in catalytic amounts (less than 2 mole %).

EXPERIMENTAL

All reagents and solvents were rigorously dried and freshly distilled before use. Polymerizations were conducted under a dry nitrogen atmosphere.

Polymerization Procedure. A flame dried resin flask was charged with the calculated weight of diol as a 50% w/w solution in methylene chloride. The solution was cooled to 0°C, and the desired amount of boron trifluoride etherate added dropwise. After stirring 1 hour the calculated amount of monomer was added as a 20% w/w solution in methylene chloride over 10 minutes. After stirring 24 hours, the solution was quenched with a

volume of saturated aqueous sodium chloride solution equal to the volume of catalyst used. The organic layer was separated, washed with an equal volume of 10% aqueous sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The organic fraction was then added to a vigorously stirred 10 fold volume excess of methanol. The resulting insoluble residue was separated and dried to constant weight under high vacuum at ambient temperature.

The disappearance of monomer was monitored using a Varian 1400 gas chromatograph equipped with a glass column packed with 10% OV-101 on chrom Q, with n-decane as an internal standard. Rates of polymerization were calculated using the assumption that all monomer consumed was converted to polymer.

Molecular Weight Determination. All molecular weights were determined using a Waters gel permeation chromatograph equipped with a differential refractive index detector and a Data Module 730. The column set consisted of seven microstyragel columns (two 100Å, two 500Å, two 10³Å, and one 10⁴Å) connected in series; the eluting solvent was tetrahydrofuran. The system was calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000. Molecular weight determinations were confirmed using a Chromatrix KMX6 light scattering analyzer.

Functionality Determination. The polyol (1 g) was heated for 15 minutes at 95°C with 2 ml of a 2:1 mixture of pyridine and acetic anhydride. The resulting solution was then added to 50 ml water, and the mixture titrated with 0.1N sodium hydroxide. The titer of the polyol solution was then compared with the titer of a blank solution containing no polyol. The difference in titer between the sample and blank was used to calculate the hydroxy functionality of the polymer.

RESULTS AND DISCUSSION

Our initial experiments with oxetanes indicated that the rate of reaction of boron trifluoride etherate and butanediol was rapid, and even in the presence of monomer formed a boron trifluoride-diol complex. We therefore preformed a 2 to 1 boron trifluoride-butanediol complex and used this to initiate the polymerization of 3, 3-bis(azidomethyl)oxetane, a monomer of considerable interest to our program. We observed that polymerization of a mixture of 1 mole boron trifluoride-butanediol complex and 16 moles of monomer, if allowed to go to completion, gave a polymer of molecular weight 2800 and a polydispersity of 1.1. The observed molecular weight was, within experimental error, equal to the sum of the molecular weights of 1 mole butanediol and 16 mole monomer (2778).

The results of experiments on the effect of diol to catalyst ratio on the polyol molecular weight are shown in Table 1. The desired molecular weights were produced when a 2/1 ratio of boron trifluoride etherate to butane diol was used. A ratio of 1/1 does not give an effective initiator, while a 3/1 ratio gives an uncontrolled polymerization forming a high molecular weight polymer, apparently due to the presence of uncomplexed catalyst. The structure of the boron trifluoride-diol complex is now being examined and will be described in a later paper.

In order to achieve a polymer with a high energy content we examined the polymerization of 3-(2,2-dinitropropoxymethyl)-3-methyloxetane. In this case we used a nitroalkanediol, 2-(2,2-dinitropropyl)-1,4-butane diol, as the initiating diol. The results of these experiments are shown in Table 2. In all cases the molecular weight of the product as determined by GPC was in agreement with the expected molecular weight. For example, the molecular weight of a polyol containing four units of monomer and 1 unit of diol is 1157. The observed molecular weight in this case was 1200. In these reactions the monomer conversion was greater than 95%, and the polydispersity was 1.1. NMR analysis of these products showed that the diol had been incorporated with the theoretical amount of monomer.

Table 1

EFFECT OF DIOL/CATALYST RATIO ON POLYOL MOLECULAR WEIGHT

Reactant Mole Ratio			Observed \bar{M}_w^*
BAMO	BDO	BF ₃	
16	2	1	No polymerization
16	1	1	No polymerization
16	1	2	2800
16	1	2.5	2800
16	1	3	3700
16	1	4	5000

* Calculated molecular weight 2778.

Table 2

CONTROLLED POLYMERIZATION OF
3-(2,2-DINITROPROPOXY METHYL)-3-METHYL OXETANE

Mole Ratio Oxetane/diol	Observed \bar{M}_w	Calculated \bar{M}_w
4/1	1200	1157
6/1	1600	1625
8/1	2000	2093

To determine if the diol was incorporated in the head of the polymer chain (a monocation), or in the middle (a dication), we conducted the following experiment. One mole of diol complex was used to initiate the polymerization of six moles of oxetane and the living cation quenched with excess diol. If a dication had been generated, then the polymer would contain six units of monomer and 3 units of diol (molecular weight 2067). If a monocation was formed then six units of monomer would be combined with two units of diol to give a molecular weight of 1846. The observed molecular weight was 1800, indicating agreement with Hammonds observation⁹ that a monocation is involved.

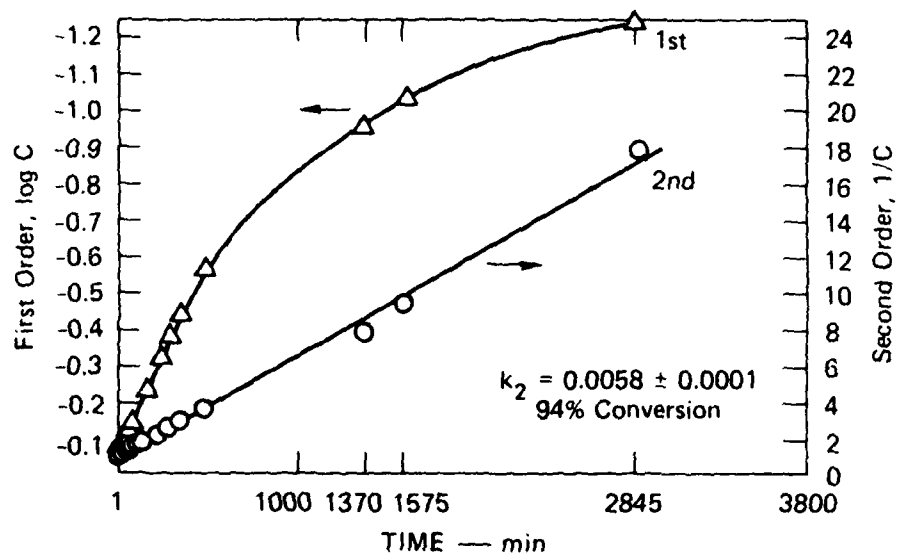
Analysis of the functionality of all polymers described in this paper showed that a theoretical value of 2 was obtained, indicating that a high degree of control of the polymerization had been achieved.

GENERAL KINETICS OF POLYMERIZATION

We examined the rate of polymerization of BAMO in an effort to elucidate the mechanism of polymerization.

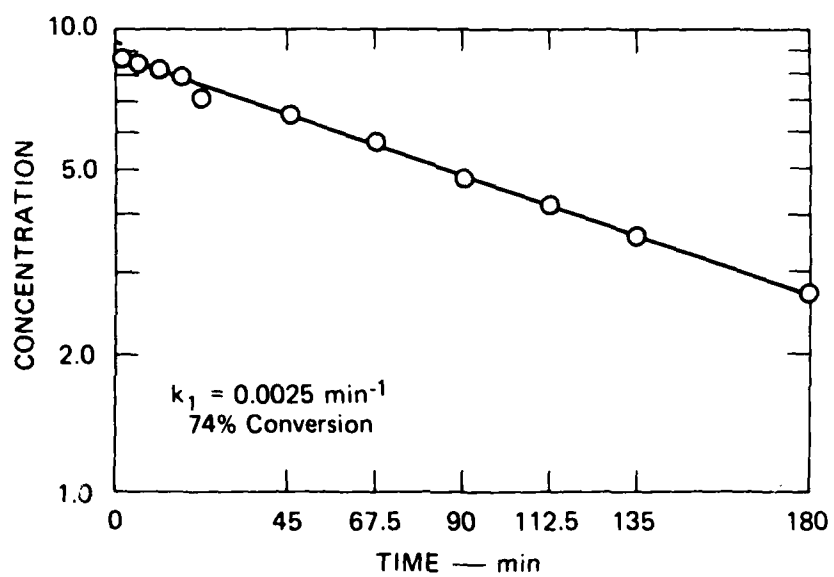
Our investigation began by determining the rate of polymerization of BAMO using the stoichiometry which gives molecular weight control, namely, a 20%wt/wt solution of BAMO (0.06 mol), 1,4-butanediol (BDO) (0.003 mol), and boron trifluoride etherate (0.006 mol) in methylene chloride. The reaction temperature was kept at 19°C during the entire polymerization. At time zero, BAMO was added to a solution of BDO, boron trifluoride etherate, and methylene chloride. The reaction was quenched after 47 hours giving a 94% conversion. The data obtained were plotted as both first and second order reactions with respect to monomer concentration, Figure 1. The graph indicates that the reaction is second order over the 94% conversion. However, if the data are plotted up to 74% conversion the reaction appears to follow first order kinetics, Figure 2.

Rose¹⁰ reports that the concentration of the cocatalyst in the polymerization affects the rate and order of the reaction. That is, the reaction changes from first to second order as the cocatalyst concentration increases. As a result of this, the rate of monomer uptake is described



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FIGURE 1 FIRST AND SECOND ORDER PLOT OF POLYMERIZATION
OF BAMO TO 94% CONVERSION



SA-8627-17

FIGURE 2 FIRST ORDER PLOT OF POLYMERIZATION OF BAMO
TO 74% CONVERSION

by the following equation, provided the cocatalyst concentration does not exceed a limiting value:

$$-d[M]/dt = \text{const.} \times [M] [BF_3] [\text{cocatalyst}]$$

where $[M]$ = monomer concentration. However, when the cocatalyst concentration exceeds the limiting value the rate expression becomes:

$$-d[M]/dt = \text{const.} \times [BF_3 \cdot M] [M]^2$$

The rate values quoted in Rose's paper¹⁰ represent conversions between 70 to 80%. However, our data show that the polymerization appears to follow first order kinetics up to 74% conversion and then changes at higher conversion. Because Rose does not report conversions as high as 94% we are not sure if his system displays the same phenomenon.

CONCLUSIONS

We have demonstrated that polyether glycols of varying, pre-determined molecular weights can be prepared by varying the stoichiometry of reactants. The molecular weight is controlled by an initiator composed of a 1/2 mole ratio of a diol and $BF_3 \cdot Et_2O$. The polymers are obtained in high yield, with low polydispersity, minimal cyclic oligomers contamination and with the desired functionality. Initial examination of the kinetics of the polymerization suggests a complex system that cannot be elucidated at this time.

ACKNOWLEDGMENTS

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Appendix B

COPOLYMERIZATION OF 3,3-BIS(AZIDOMETHYL) OXETANE WITH TETRAHYDROFURAN

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SYNOPSIS

The objective of the work was to synthesize energetic prepolymers for use in the formation of elastomeric binders for use in propellant and explosive compositions. The copolymerization of 3,3-bis(azidomethyl) oxetane (BAMO) with tetrahydrofuran (THF), using boron trifluoride etherate/1,4-butanediol complex as initiator was studied as a function of the ratio of BAMO to THF. The 50/50 mole percent oligomer was converted to a gumstock by reaction with trimethylolethane and tolylene diisocyanate. The tensile strength (engineering) of the gumstock at break of 7.93×10^6 dyne/cm² (115 psi) was obtained at an elongation of 425%. The monomer reactivity ratios, r_1 (THF) = 0.44 ± 0.17 and r_2 (BAMO) = 1.73 ± 0.24 , were determined by the Kelen-Tudos method.

INTRODUCTION

Low molecular weight (2000 to 4000) hydroxy-terminated polymers are required to form elastomeric binders for use in propellant and explosive formulations. The ideal prepolymer would be an inexpensive, stable, amorphous, flexible material with a glass transition temperature (T_g) below -60°C and a positive heat of formation. Polyethylene and polypropylene glycols are among the oligomers currently used in binder formation. Although these polyether glycols have many of the necessary properties, such as good chemical and thermal stability, high degree of flexibility and low T_g , they have a negative heat of formation. Consequently they detract from the overall energy of the formulation.

The successful synthesis of a prepolymer with a positive heat of formation that also possesses the necessary mechanical properties would represent a significant advance.

EXPERIMENTAL

Materials. Burdick and Jackson UV grade THF was dried by storing over 4A molecular sieve. Commercial grade boron trifluoride etherate was freshly distilled in vacuo prior to use. 1,4-butanediol was distilled from calcium hydride and stored over 4A molecular sieve.

3,3-Bis(azidomethyl)oxetane (BAMO) was prepared by heating a solution of one mole 3,3-bis(chloromethyl)oxetane and two moles sodium azide in dimethylformamide at 80°C for 18 hours. After cooling, the precipitated sodium chloride was removed by filtration and the filtrate vacuum distilled to give 130 g (80% yield) of BAMO, bp 78°C/0.2 Torr. CAUTION: Allowing the hot pot residue to contact air resulted in a violent detonation. Frankel has reported the purification of BAMO by column chromatography (methylene chloride, basic alumina)³, which is the method of choice.

Polymerization Procedure. The copolymerizations were run in a jacketed 100-ml glass resin flask equipped with a mechanical stirrer. In each case 0.25 moles of monomer, 0.025 moles BF_3 etherate, and 0.0125 moles butanediol were used. The THF, butanediol, and BF_3 etherate were combined and stirred for 30 minutes. The reaction mixture was then cooled to -5°C and the BAMO added. After stirring for 48 hours, the reaction was quenched with saturated aqueous sodium chloride. The crude polymer was separated, dissolved in a minimum volume of methylene chloride and reprecipitated by addition of a tenfold volume of methanol. The reprecipitated polymer was isolated by decanting the methanol and drying in vacuo.

Molecular Weight Determination. Number average and weight average molecular weights of poly-BAMO/THF were determined using a Waters gel-permeation chromatograph equipped with four microstyragel columns (100 Å, 500 Å, 10^3 Å, 10^4 Å), a differential refractive index detector, and a Data Module 730. The columns were calibrated with polypropylene glycol standards of molecular weight 800, 1200, 2000, and 4000.

Measurements of Reactivity Ratios. The reactivity ratios of THF and BAMO were determined by the Kelen-Tudos method.⁴ The disappearance of monomer was monitored by gas chromatography, using a glass column packed with 10% OV-101 on Chrom Q. Samples were periodically removed from the reaction mixture and quenched by dissolution in wet methylene chloride. At the end of the reaction the copolymer was isolated and purified as described above and characterized by its NMR spectrum and elemental analysis.

RESULTS AND DISCUSSION

The objective of the work described here was to develop a binder system that would not detract from the overall energy of the formulation. To this end we examined the synthesis of polyether glycols with positive heats of formation. One approach would be the cationic polymerization of azido or nitro-substituted oxetanes. However, earlier investigations have shown that homopolymers prepared from substituted oxetanes have unacceptably high T_g values.¹ One approach to lowering the T_g values of these materials would be to interrupt the symmetry of the polymer by copolymerization of dissimilar monomers. Therefore, we investigated the copolymerization of oxetanes with tetrahydrofuran (THF). We chose THF because it forms a polyether, is known to copolymerize with oxetane,² and should impart a low T_g to the copolymer. We have found that 3,3-bis(azidomethyl)oxetane (BAMO) is a promising oxetane monomer for binder applications. Therefore, we investigated the copolymerization of BAMO with THF.

The copolymerization of BAMO and THF was accomplished as described in the experimental section. To determine the effect of THF incorporation on the physical properties of the copolymer, a series of copolymerizations was run in which the initial ratio of BAMO to THF was varied. The properties of the polymers obtained from these copolymerizations are shown in Table 1.

Table 1
POLYMER PROPERTIES OF BAMO/THF

Mole Fraction of Monomer Charge		Mp	Density	Functionality	Molecular Weight
BAMO	THF	°C	g/cc	-OH/molecule	\bar{M}_w
1.00	0	78	1.30	1.9	6500
0.75	0.25	50	1.24	2.0	6900
0.60	0.40	25	1.27	2.0	6200
0.50	0.50	<0	1.18	2.0	7300

The copolymerization of BAMO and THF yields low molecular weight oligomers with melting points lower than that of the BAMO homopolymer. The 50/50 mole % copolymer is a mobile oil at ambient temperature, and its viscosity is relatively low compared to polymers of higher BAMO content. The 50/50 copolymer had the best overall physical properties for a binder application.

A gumstock was prepared from the 50/50 copolymer by mixing with trimethylolethane to achieve the required crosslink density of 10% and then condensed with one equivalent of tolylene diisocyanate. The sample was cured for 24 hours at 65°C.

The room temperature stress/strain curve of the 50/50 copolymer gumstock obtained at a strain rate of 0.02 in./min, gave an engineering stress at break of 7.93×10^6 dyne/cm² (115 psi). Elongations of up to 425% were observed. Equilibrium swelling measurements in THF gave an average molecular weight between crosslinks of about 89,000. Dynamic tensile moduli measurements at 110 hz indicated that the T_g of the gumstock was -56°C. Differential scanning calorimetry (20°C/min) showed only a single exotherm that began at 210°C and reached a maximum at 254°C.

To better characterize the copolymer composition and polymerization mechanism, the reactivity ratios of BAMO and THF were determined using the Kelen and Tudos (KT) improved linear graphic method.³ The KT method is an approximation that does not integrate the differential copolymerization equation (1).

$$\frac{dm_1}{dm_2} = \frac{m_1}{m_2} \frac{1 + r_1 m_1/m_2}{R_2 + m_1/m_2} \quad (1)$$

Because of this, the method is strictly valid only at very low conversions. However, the extended KT method has a conversion compensation factor that allows it to be used with high conversions. We used this compensation factor because the rates of cationic polymerizations are very high, and stopping the reaction at sufficiently low conversion is often impossible.

The KT equation (equation 2) is derived from equation 1 by a series

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (2)$$

of assumptions that are beyond the scope of this paper. Eta and Xi are calculated from experimental data as shown in Scheme 1, r_1 and r_2 are the reactivity ratios, and alpha is an arbitrary constant. In Scheme 1, ζ_1 and ζ_2 are the partial molar monomer conversions, dm_1/dm_2 is the experimentally determined average copolymer composition, and alpha is an arbitrary constant that uniformly distributes the experimental points between 0 and 1.

Scheme 1

$$\xi = \frac{F}{\alpha + F}, \quad \eta = \frac{G}{\alpha + F}$$

where

$$F = \frac{dm_1/dm_2}{\frac{\log(1-\zeta_1)}{\log(1-\zeta_2)}}^2, \quad G = \frac{dm_1/dm_2 - 1}{\frac{\log(1-\zeta_1)}{\log(1-\zeta_2)}}$$

and

$$\alpha = (F_{\max}/F_{\min})^{1/2}$$

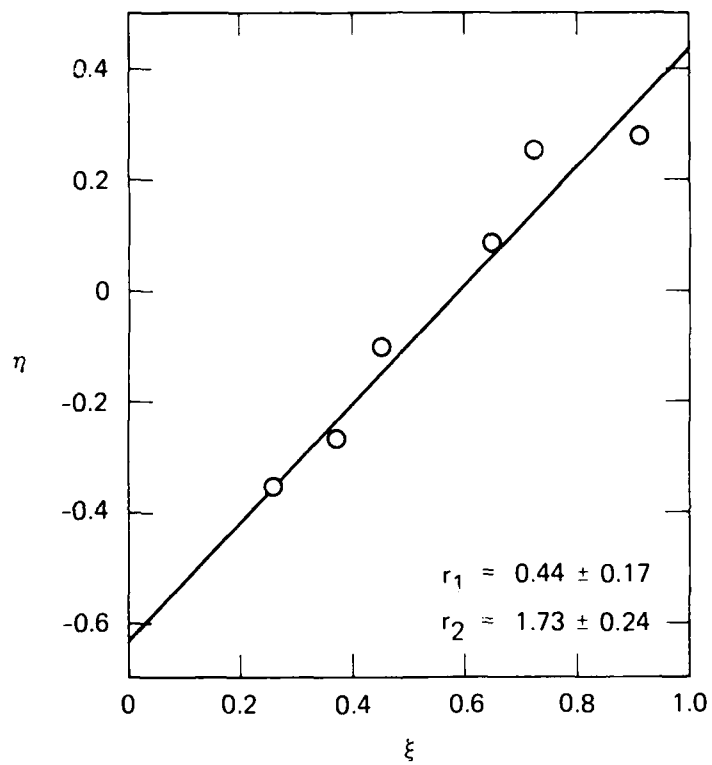
If a plot of η versus X_1 is linear, then the copolymerization is binary, and the slope of the plot is equal to $r_1 - r_2/\alpha$ and the y intercept equal to $-r_2/\alpha$. Since α is an arbitrary constant selected by the experimenter, r_1 and r_2 can then be calculated.

Table 2 shows the averaged η and X_1 values obtained from a series of copolymerizations of BAMO and THF. Since a plot of η versus X_1 for this series is linear (Figure 1), the BAMO/THF copolymerization system is binary. The calculated reactivity ratios are r_1 (THF) = 0.44 ± 0.17 and r_2 (BAMO) = 1.73 ± 0.24 .

Table 2

η and ξ PARAMETERS
 $\alpha = 2.79$

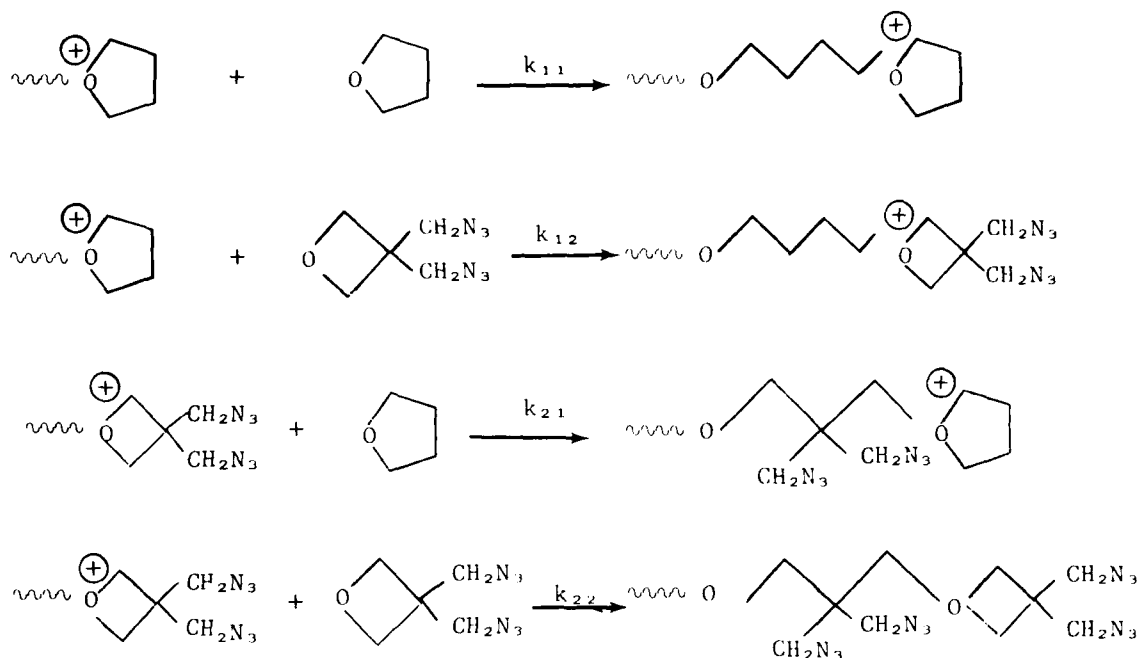
Mole fraction of THF/BAMO in Charge	Mole fraction of THF/BAMO in Copolymer	ξ	η
0.90/0.10	0.78/0.22	0.90 ± 0.02	0.25 ± 0.07
0.80/0.20	0.70/0.03	0.72 ± 0.05	0.25 ± 0.08
0.70/0.30	0.56/0.44	0.65 ± 0.07	0.08 ± 0.09
0.50/0.50	0.39/0.61	0.43 ± 0.04	-0.13 ± 0.02
0.40/0.60	0.28/0.72	0.38 ± 0.02	-0.27 ± 0.02
0.30/0.70	0.24/0.76	0.29 ± 0.02	-0.33 ± 0.03



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FIGURE 1 Eta VERSUS Xi PLOT FOR BAMO/THF ($\alpha = 2.786$)

The reactions involved in the cationic copolymerization of THF with BAMO are shown in Scheme 2. The following relationships between the rate



Scheme 2

constants of these reactions can be derived from the monomer reactivity ratios:

1. $k_{11}/k_{12} = 0.44$
2. $k_{22}/k_{21} = 1.73$

The rate of reaction of THF oxonium ion with THF monomer is less than half the rate of reaction of THF oxonium ion with BAMO monomer. Similarly, the rate of reaction of BAMO oxonium ion with BAMO monomer is 1.75 times faster than the rate of reaction of BAMO oxonium ion with THF monomer. Because of this difference in monomer reactivity ratios, BAMO/THF copolymers are not totally random.

The instantaneous polymer composition as a function of monomer feed can be plotted when the reactivity ratios of the monomers in the copolymerization are known. Figure 2 shows such a plot for BAMO/THF, where the abscissa is the mole fraction of THF in the monomer charge (f_1) and the ordinate is the mole fraction of THF in the initial polymer formed.

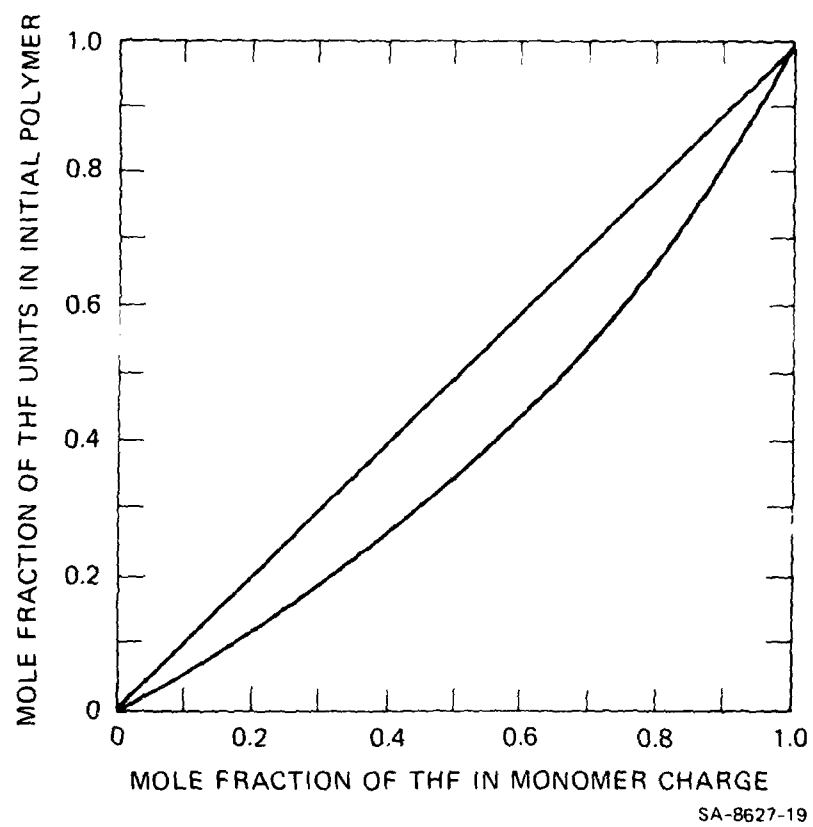


FIGURE 2 INSTANTANEOUS COMPOSITION OF BAMO/THF COPOLYMER
AS A FUNCTION OF THE MONOMER CHARGE

The plot indicates that the BAMO/THF system can form polymers containing a significant concentration of each monomer over a considerable range of monomer mixtures. This degree of incorporation of THF and BAMO in the copolymer makes possible the preparation of well defined copolymers with respect to composition and molecular weight that have both a low degree of crystallinity and low glass transition temperatures.

CONCLUSIONS

Cationic copolymerization of BAMO and THF with a BF_3 etherate butane diol complex produces hydroxy terminated polyethers whose average molecular weight is a function of the mole ratio of initiator complex to monomer. The physical properties of BAMO/THF copolymers can be varied by changing the ratio of BAMO to THF in the monomer feed. Low melting (less than 0°C) high energy hydroxy terminated prepolymers for use in binder applications may be prepared by this method. Reactivity ratios generated by the Kelen-Tudos method indicate that the copolymerization of BAMO and THF proceeds by a binary mechanism.

ACKNOWLEDGMENT

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Appendix C

A NEW POLYMERIZATION TECHNIQUE FOR PREPARING LOW MOLECULAR WEIGHT POLYETHER GLYCOLS*

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Presented at the 1981 JANNAF Propulsion Meeting
New Orleans, Louisiana, 27th May 1981

ABSTRACT

We have demonstrated that exact and predetermined molecular weight polyols derived from the cationic polymerization of cyclic ethers can be obtained by using stoichiometric quantities of diol to monomer. The final molecular weight achieved is proportional to the stoichiometric addition of the molecular weights of the diol and cyclic ether. We have further demonstrated that liquid polyols are produced when a monomer that gives a crystalline homopolymer, is copolymerized with tetrahydrofuran. In both studies the polyols were found to have theoretical functionalities of 2 and minimal cyclic oligomer content.

INTRODUCTION AND BACKGROUND

The overall objective of our research was to produce energetic polyols from cyclic ethers that incorporated the following properties:

- Molecular weight control
- Reproducible molecular weight
- No cyclic oligomer contamination
- Hydroxy functionality of 2.0
- Low polydispersity (1.1 to 1.2)
- Liquid at $\leq 50^{\circ}\text{C}$
- Glass transition temperature less than -60°C .

In an effort to produce low molecular weight polyols (2000-4000), the polymerization of 3-(2-fluoro-2,2-dinitroethoxymethyl)-3-methyl oxetane (FOE) using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst was conducted. The results of this work are given in Table I.

Run 1 was used as a starting point for catalyst loading to obtain relatively low molecular weight products. Methods investigated to lower the molecular weight further included increasing the catalyst loading, using water as a co-catalyst, and raising the polymerization temperature. All these parameters effectively increase the competing termination reactions. Only Run 3, using an equal amount of catalyst to water, had a noticeable effect on decreasing the polyol molecular weight. However, it also had a detrimental effect on polymer yield. Almost 80% of the monomer was recovered. Except for this run, the molecular weights recorded were in the range of 5000 to 6000. The GPC data also showed a major contaminant, which was identified as the FOE cyclic tetramer. A typical GPC trace is shown in Figure 1.

*This work was supported by the Office of Naval Research Contract N00014-79-C-0525.

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Table I. POLYMERIZATION RUNS FOR FOE

Run	Temperature (°C)	Reactants			GPC Analysis ^a		Molecular Weight	
		Monomer	(parts by weight) BF ₃ ·Et ₂ O	H ₂ O	Polymer Elution Volume (ml)	% Yield ^b	M _n (000)	M _w (000) Q ^d
1 ^c	20	100	3	0	42	92.3	3.126	6.662 2.13
2	20	100	20	0	43	83.0	--	5.4 --
3	20	100	10	10	52	14.8	--	1.3 --
4	20	100	10	1	43.5	82.0	--	5.0 --
5	40	100	10	1	43.8	87.6	--	4.4 --

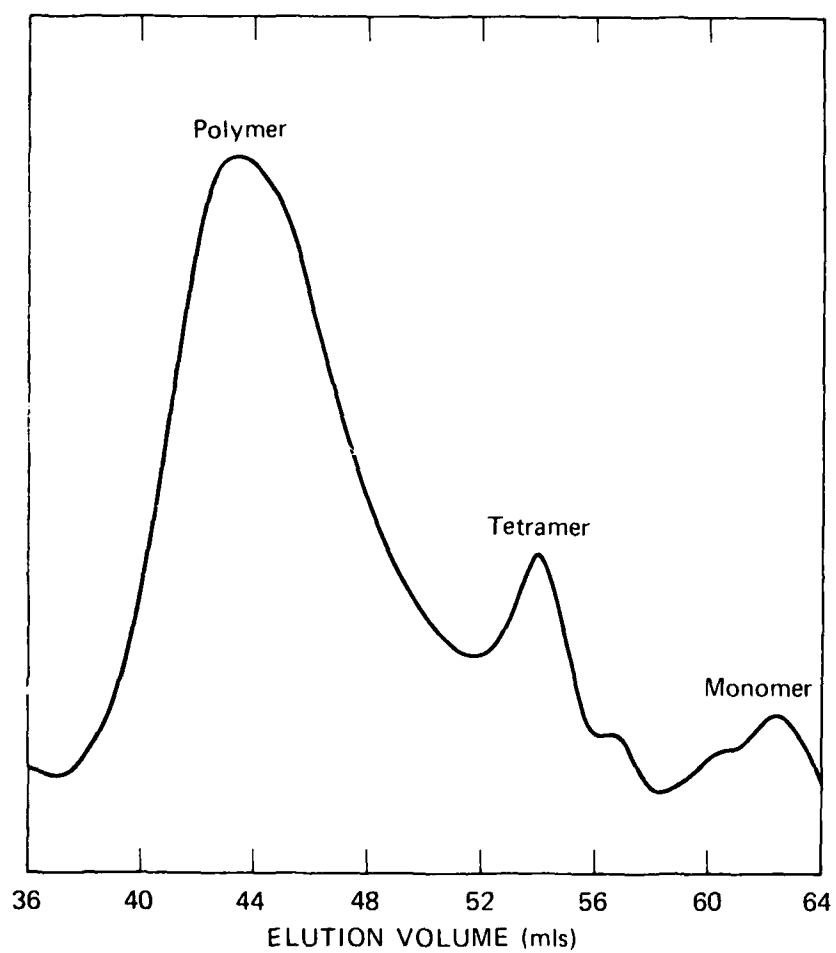
2

^a Analyzed using a Waters Associates GPC with THF on microstyragel columns (two 100 Å, two 500 Å, one 10⁻³ Å, one 10⁻⁴ Å, one 10⁻⁵ Å).

^b The balance of recovered material was unreacted monomer (elution volume: 61.5 ml).

^c Analysis by Chromatix KMX6 light scattering analyzer attached to the effluent. All other molecular weights determined by comparison to polypropyleneglycol standards.

^d Polydispersity, $Q = \frac{M_w}{M_n}$



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FIGURE 1 GPC OF FOE POLYMERIZATION

We concluded that the methods used in the above study would not produce polyols in high yield or in the molecular weight range desired. Furthermore, without additional research the state of the art of cationic polymerization of cyclic ethers was inadequate¹⁻⁴ to permit the synthesis of polyols with the requisite properties.

High molecular weight polymers are obtained if a small number of initiating species is formed during the initial stage of polymerization. Since the objective of this research was to produce low molecular weight oligomers, we postulated that increasing the number of initiating species would limit the molecular weight of the final polyol. That is, the molecular weight would be determined by the ratio of initiator to monomer.

RESULTS AND DISCUSSION

The reported use of catalytic amounts of diols as co-catalysts with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ has been studied⁵⁻⁹ extensively. Inclusion of the diol in the polymer was observed in many cases. Hammond et al.¹⁰ noted that lower molecular weights were obtained at low conversion when the diol loading was increased from 0.08 to 1.65 mol%.

We postulated that the reactivity ratio of the cyclic ether to diol would favor preferential reaction of the diol with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to form a complex. If this complex could initiate cationic polymerization, then a large number of initiator species could be generated. The molecular weight of the polyol would then be directly proportional to the direct addition of the stoichiometric molecular weights of the diol and monomer.

HOMOPOLYMERIZATION

To test the hypothesis a series of polymerizations using 3-(2,2-dinitropropoxymethyl)-3-methyl oxetane (oxether-1) and 2-(2,2-dinitropropyl)-1,4-butanediol (DNPBDO) were conducted, as shown in Table II. In all cases

Table II. CONTROLLED POLYMERIZATION OF OXETHER-1

Mol Ratio Oxether-1/DNPBDO ¹	Observed M.W. \bar{M}_w (000)	Calculated M.W. \bar{M}_w (000)
4:1	1.2	1.157
6:1	1.6	1.625
8:1	2.0	2.093

¹6% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ based on monomer

the molecular weight observed by GPC analysis was consistent with the calculated molecular weight. For example, four moles of oxether-1 and one mole of DNPBDO gives a calculated molecular weight of 1157. The observed molecular weight of the polyol was 1200. Two other oxetane monomers, 3,3-bis(azidomethyl) oxetane (BAMO) and FOE, and a second diol, 1,4-butanediol (BDO) were examined under the same conditions, and similar results were obtained.

A study was then initiated to determine the range of catalyst to diol ratios that may be used. The model system studied was BAMO and BDO. The effect of varying the mole ratio of BDO to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at a constant monomer ratio is shown in Table III. The results indicate that the preferred diol/catalyst

Table III. EFFECT OF DIOL/CATALYST RATIO
ON POLYOL MOLECULAR WEIGHT

BAMO	Reactant Mole Ratio		Observed* \bar{M}_w (000)
	BDO	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	
16	2	1	No polymerization
16	1	1	No polymerization
16	1	1.5	2.8
16	1	2	2.8
16	1	3	3.7
16	1	4	5.0

* Calculated molecular weight = 2778.

ratio is 1/2. It is interesting to note that a ratio of 1/1 does not initiate polymerization, and a ratio greater than 1/3 suggests that uncombined catalyst is present and initiates a competing, uncontrolled polymerization.

Because of its importance to the ongoing energetic polymer research program, BAMO was selected as the preferred monomer to investigate the effect of molecular weight on physical properties. A series of polyols was prepared with molecular weights ranging from 2000 to 6000. We found that the melting point was not affected by changing the molecular weight. For example, a molecular weight of 6000 gave a melting point of -78°C whereas molecular weight 2000 gave a melting point of -76°C . The functionality of these polyols was found to have a theoretical value of 2. As our objective was to produce a liquid polyol at room temperature, we concluded that this could not be met by homopolymerization of BAMO.

The physical properties of polyols are dependent on the crystallinity of the macromolecule, which in turn is a function of the symmetry of the macromole or repeating unit (monomer). Therefore, a homopolymer will tend to be more crystalline than a copolymer containing dissimilar monomers. Thus, lowering of crystallinity will reduce the melting point and Tg of the system. Because BAMO would not yield a liquid polyol, we investigated its copolymerization.

COPOLYMERIZATION

To demonstrate the effect of lower crystallinity on melting point, we conducted a series of copolymerizations of BAMO and tetrahydrofuran (THF).

The results of our investigation of three copolymer systems compared to poly-BAMO are given in Table IV. The results show the effect of the lowering

Table IV. EFFECT OF BAMO/THF MONOMER RATIO
ON PHYSICAL PROPERTIES

Polyol BAMO/THF mol %	Molecular Weight \bar{M}_w	Melting Point, °C	Density, g/cc	ΔH_f kcal/100g ¹ , est	Functionality
100/-	6500	78	1.3	+60	1.92
75/25	6900	50	1.245	+42	1.96
60/40	6300	25	1.21	+28	1.95
50/50	7300	-5	1.180	+17	1.99

of melting point by incorporating THF as a comonomer. A melting point of 50°C for the 75/25 mol% BAMO/THF is comparable to PEG 4000 (m.p. 55°C), a widely used polyol which is processible. Furthermore, the BAMO/THF polyol has the added improvement of increased energy content over PEG. A GPC trace of a 50/50 mol% BAMO/THF polyol is shown in Figure 2.

Work is now underway to prepare gum stocks from these polyols for subsequent physical testing. Preliminary DSC data show good thermal stability with an exotherm onset at 200° with a peak at 250°C.

CONCLUSIONS

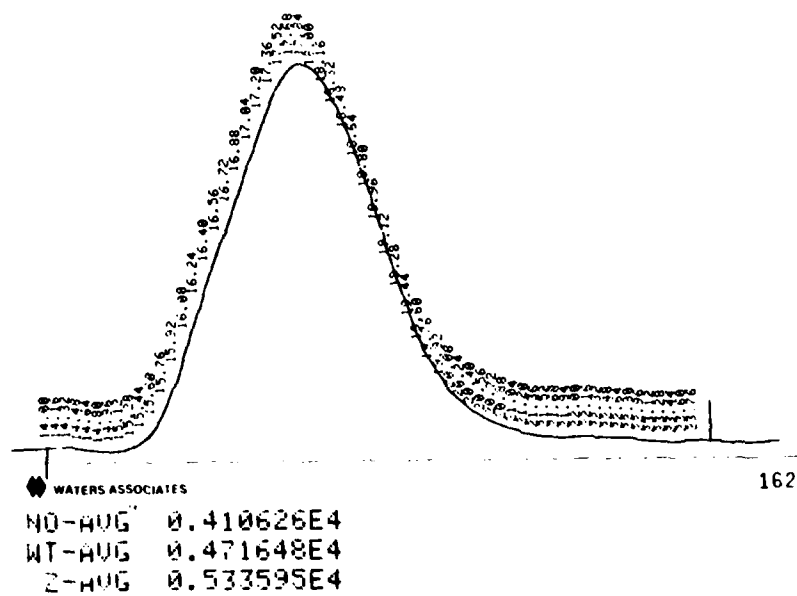
We have demonstrated that polyether glycols of varying, predetermined molecular weights can be prepared by varying the stoichiometry of reactants. Molecular weight is controlled by generation of an initiating species from a complex derived from a diol and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The polyols are prepared in high yield, low polydispersity, theoretical functionality, and contain minimum cyclic oligomer.

A monomer (BAMO) which gives a crystalline homopolymer was copolymerized with tetrahydrofuran to produce low melting polyols that can be processed at ambient temperature into highly elastomeric, cured gum stocks.

EXPERIMENTAL

HOMOPOLYMERIZATION

To a flame dried resin flask was added a known weight of cyclic ether as a 20% w/w solution in dried methylene chloride. A calculated weight of the diol was then introduced and the solution stirred at room temperature for 10 minutes. A calculated weight of freshly distilled $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was then added and the reaction ran for 6 hours. The polymerization was quenched with a volume of saturated aqueous sodium chloride solution equal to the volume of



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FIGURE 2 GPC OF 50/50 mol% BAMO/THF COPOLYMER

catalyst added. The organic layer was removed, washed with 10% sodium bicarbonate solution and dried over magnesium sulfate.

COPOLYMERIZATION

To a flame dried resin flask was added a known weight of tetrahydrofuran under a nitrogen atmosphere. A calculated weight of diol and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was then added. After 10 minutes mixing the solution was cooled to -5°C and the temperature was maintained at -5°C until the polymerization was quenched. The comonomer was then introduced to the flask and the polymerization allowed to run for 18 hours. An equal volume of dried methylene chloride was added to the flask, and after dissolution of the polymer was observed it was quenched with a volume of a saturated aqueous sodium chloride equal to the volume of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ used. The polymer solution was then warmed to room temperature, and the organic layer removed. The organic layer was then washed with 10% sodium bicarbonate solution and dried over magnesium sulfate.

POLYMER PURIFICATION

The methylene chloride solution of polymer was added slowly to a vigorously stirred ten-volume excess of anhydrous methanol. The insoluble residue was removed and dried on a high vacuum line at room temperature.

MOLECULAR WEIGHT DETERMINATION

All molecular weights were determined by gel permeation chromatography. The column set consisted of seven microstyrigel columns (two 100 Å two 500 Å, one 10^3 Å one 10^4 Å, and one 10^5 Å), and the solvent used was tetrahydrofuran. The system was calibrated with molecular weight 800, 1200, 2000, and 4000 polypropylene glycol standards. The data from the refractive index detector was processed by a Waters Associates Data Module 730. Molecular weights determined in this manner were confirmed using a Chromatix KMX6 light scattering analyzer.

FUNCTIONALITY

The polyol (1 g) was treated with 2 ml of a standard acetylating agent (66 ml pyridine/33 ml acetic anhydride) for 15 minutes at 95°C . Each analysis was then compared with a blank by titrating with 0.1 N sodium hydroxide. The difference in titrant between the sample and the blank was used to calculate the hydroxyl equivalent weight of the polyol.

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Appendix D

BAMO/THF COPOLYMER: A CANDIDATE ENERGETIC POLYETHER GLYCOL

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Presented at

Symposium on the Chemistry of the Synthesis and
Characterization of Energetic Monomers and Prepolymers

The Johns Hopkins University
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21 July 1981

We have demonstrated that exact and predetermined molecular weight polyols derived from the cationic polymerization of cyclic ethers can be obtained by using stoichiometric quantities of diol to monomer. The final molecular weight achieved is proportional to the stoichiometric addition of the molecular weights of the diol and cyclic ether. We have further demonstrated that liquid polyols are produced when a monomer that gives a crystalline homopolymer, is copolymerized with tetrahydrofuran. In both studies the polyols were found to have theoretical functionalities of 2 and minimal cyclic oligomer content.

The overall objective of our research is to polymerize cyclic ethers to produce energetic polyols with the following characteristics:

- Molecular weight control
- Reproducible molecular weight
- No cyclic oligomer contamination
- Hydroxy functionality of 2.0
- Low polydispersity (1.1 to 1.2)
- Liquid at $\leq 50^{\circ}\text{C}$
- Glass transition temperature less than -60°C .

An extensive investigation of the homopolymerization of 3,3-bis(azidomethyl)oxetane [BAMO] showed conclusively that the resultant polymer melting range was relatively independent of molecular weight. Over the molecular weight range of interest (1200

to 6500) the melting range of BAMO polyols was $78 \pm 4^\circ\text{C}$, which is considered marginal for processing by standard nonsolvent techniques. Also, to obtain polymers with glass transition temperature $< -40^\circ\text{C}$, we found it necessary to copolymerize BAMO with a dissimilar monomer to provide less "crystalline materials." Consequently, we conducted a series of copolymerizations of BAMO and tetrahydrofuran [THF] and found a dramatic lowering of the melting range; the minimum was -5°C obtained with a 50/50 mole ratio of monomers.

The aforementioned system was examined for the rate of monomer uptake. After 20 hours BAMO had achieved a steady state of 98% conversion, whereas THF required 38 hours to reach 85% conversion. The reactivity ratios of BAMO and THF were found to be 1.40 and 0.31, respectively. A molecular weight of 4,000 was used for this co-polymerization study; a polydispersity of 1.1 and a functionality of 2.0 was observed on analysis of all polymers. Gumstocks were then prepared from the 50/50 BAMO/THF polymer by curing with tolylene diisocyanate, and the crosslink density was controlled by adding the required amount of trimethylol ethane.

The stress/strain curve, obtained by Instron analysis, gave a value of 115 psi at 425% elongation. An average of 89,000 molecular weight units between crosslinks was determined by swelling experiments. A Rheovibron study showed a classical E' curve for an elastomer and the E'' curve showed a single glass transition temperature of -54°C . The tan delta plot produced a value of over 1.5 from -60 to -30°C indicating a surprising ability to absorb a large amount of energy at this low temperature. Differential scanning calorimetry showed a flat trace until onset of an exotherm at 210°C , maximizing at 254°C .

At this point of our investigation it appears that a copolymer of BAMO/THF is a viable candidate system that provides good low temperature and elastomeric properties and thermal stability over the projected operating temperature.

In order to achieve a polymer containing a higher energy content over BAMO/THF, we have begun to examine the copolymerization of BAMO with other azido monomers. Two candidate comonomers, namely 3-azidomethyl tetrahydrofuran (AMTHF) and 3-azido oxetane (AO) are available for this study. The synthesis of AMTHF has been completed by us, and AO was prepared by Dr. K. Baum at Fluorochem. Preliminary data on a copolymer obtained from 50/50 mol% BAMO/AO indicate that a liquid polymer is produced at a molecular weight of 3,000. This particular system is being scaled up so that gumstocks may be produced for testing.

We wish to acknowledge the following SRI personnel who contributed to the effort described here: Robert L. Simon, Steven J. Staats, John M. Guimont, David P. Cotts, and Donald L. Ross. We also wish to acknowledge the valuable suggestions of Dr. R. S. Miller, the project monitor. This research was supported by the Office of Naval Research, Contract N00014-79-C-0525.

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